

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Nickel-Chromium-Cobalt Alloys

We, ROLLS-ROYCE LIMITED, a British Company, of Nightingale Road, Derby, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Difficulties are experienced in the manufacture of the inner walls of jet pipes of modern gas turbine engines. Such walls must be made of an alloy which will stand up to repeated and rapid heating up to and cooling from temperatures which have today increased to about 800° C. The alloy must have a high resistance to oxidation, must be readily weldable, possess a high creep strength and have good tensile strength and ductility to stand up to the stresses involved in such pipes which may be as much as 40 inches in diameter and 20 feet in length.

The effect of the increase of temperature has shortened the life of the materials previously employed and stronger known alloys which the applicants have tried have shown poor ductility in or near the weld in spite of the use of various heat treatments. Moreover to apply heat treatment to the completed welded part is a matter of some difficulty in view of the dimensions of the pipe.

According therefore to the present invention there is provided an alloy having the following percentage composition by weight:—

Chromium	19.0—23%
Cobalt	12.0—25%
Molybdenum	4.72—8.6%
Titanium	1.7—2.45%
Aluminium	0.3—0.74%
Manganese	0.2—0.6%
Silicon	0.1—0.5%

and optionally up to 0.06% carbon, up to [Price 3s. 6d.]

1.0% iron, and up to 0.5% zirconium, the balance being nickel apart from impurities and residuals from deoxidisers, the molybdenum-titanium-aluminium factor of the alloy, as hereinafter defined, being at least 16.

The term "molybdenum-titanium-aluminium" factor, as used in this specification, is to be understood to indicate the factor obtained by adding together the percentage of molybdenum, twice the percentage of aluminium and four times the percentage of titanium present in the alloy.

Thus, for example, if an alloy in accordance with the present invention contains 6.1% molybdenum, 0.4% aluminium, and 2.4% titanium, its molybdenum-titanium-aluminium factor will be

$$\begin{aligned} & 6.1 + 2 (0.4) + 4 (2.4) \\ & = 6.1 + 0.8 + 9.6 \\ & = 16.5 \end{aligned}$$

Alloys according to the present invention may be extruded, e.g. into rod form, and may be forged. The alloys are, however, particularly well suited for fabrication into sheets which may be welded together to form articles such, for example, as gas turbine jet pipes and combustion chamber flame tubes of gas turbine engines. Thus these alloys have both the high ductility which is necessary to permit them to be welded and at the same time have good strength and elongation characteristics coupled with good creep resistance.

Preferably the aluminium content of the alloys is from 0.35—0.6% by weight, the titanium content is from 1.9—2.45% by weight, and the combined aluminium-titanium content is from 2.5 to 2.8% by weight.

Zirconium may be present in the alloy up to 0.5% by weight but is preferably kept low or is absent from the alloy. Similarly sulphur may be present in the alloy up to 0.01% by weight, but is preferably kept below 0.005%.

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by weight.

Carbon and iron will be present if commercial alloys are used in making up an alloy according to the present invention. We prefer, however, to keep the carbon and iron content as low as possible.

If desired, the alloy may contain 4.72%—6.1% molybdenum by weight although the preferred molybdenum content of the alloy is from 5.5—6.5% by weight.

The cobalt content of the alloy is preferably in the range 18—21% by weight.

The aluminium, manganese and silicon content of the alloys according to the present invention is of considerable importance.

Thus if the aluminium content of the alloy exceeds 0.74% by weight, the ductility of the alloy falls and its welding properties become worse because of skin formation, especially when welding sheets of the alloy. On the other hand, if the aluminium content of the alloy is less than 0.3% the creep resistance falls and is erratic.

0.2—0.6% manganese by weight and 0.1—0.5% by weight of silicon are employed so as to strengthen the alloy and improve its welding properties. These percentages of manganese and silicon make the alloy flow better and prevent bubble formation during argon arc welding. It should be appreciated that such bubbles tend to form in the weld during argon arc welding and reduce weld strength.

Molybdenum is used in the alloy of the present invention in order to give the alloy ductility. Molybdenum produces this effect by influencing the precipitation of a nickel/titanium/aluminium compound which is the main hardening constituent in the alloy. Thus as the molybdenum content of the alloy is increased, the alloy becomes stronger but less ductile, whilst as the molybdenum content of the alloy is reduced the alloy becomes weaker but more ductile.

We have found that if the molybdenum content of the alloy is from 4.72 to 8.6% by weight, the alloy has sufficient ductility to enable sheets of the alloy to be welded together and, at the same time, is sufficiently strong at high temperatures to stand up to the arduous conditions under which the jet pipes of gas turbine engines operate.

The invention is illustrated in the drawings of which Figure 1 accompanied the Provisional Specification of Application No. 38217/58 and Figure 2 accompanied the Provisional Specification of Application No. 16721/59. In these drawings:—

Figure 1 is a diagrammatic perspective view of an apparatus for testing alloys according to the present invention, and

Figure 2 is a diagram illustrating the composition of alloys according to the present invention.

TESTS.

1. Heating and Cooling:

A welded sheet of the alloy prepared for test is subjected in the weld area to heating for 10 seconds followed by natural cooling for 50 seconds while stressed at a constant load of 7.8 tons per square inch. The weld area must withstand at least 500 cycles of heating up to any temperature not exceeding 800° C. and cooling down again without failure.

An example of apparatus for carrying out this test is illustrated diagrammatically in Figure 1 in which 10 is a test piece 4 inches wide consisting of two pieces of sheet welded together at 11. The test piece 10 is suspended from a rod 12 and supports at its bottom a rod 13 carrying a weight 14.

A burner 15, which is fed through a pipe 16 with a mixture of air and gas derived from pipes 17 and 18 respectively, discharges a number of jet flames against the weld area. Around the burner 15 is a cylinder 19 having a cut away portion 20. The cylinder 19 is rotated so that the exposure of the weld to the flame lasts for 10 seconds, and for the remainder of the rotation of the cylinder, which lasts for 50 seconds, the weld is masked by the cylinder from the flame. A thermocouple 21 records the temperature of the weld. In this way the test piece can be brought up to the desired temperature, cooled naturally, and heated again rapidly to the test temperature.

2. Ductility:

The ductility of the welded test piece after being aged and stressed with the weld at right angles to the axis of pull shall be not less than 5.0% elongation after fracture of a standard size tensile test piece at a test temperature of 775° C. measured when cold on a 1.0 inch gauge length across the weld.

By standard size test piece is meant a piece 0.75 inches wide with a parallel section 3 to 3.5 inches long streamlined into ends of 1.25 inches wide.

3. Creep:

Under a continuous loading test the material shall deform by not greater than 1.0% strain after 100 hours at 775° C. under a stress of 7.8 tons per square inch.

4. Tensile strength:

The tensile strength after 30 minutes soaking and then tested at 775° C. shall be not less than 30 tons per square inch with a 0.1 proof stress of at least 14.5 tons per square inch.

Alloys according to the present invention will pass all four of the above tests.

Referring now to Figure 2, the rectangle ABCD defines the limits of the aluminium and titanium content of alloys according to the present invention with molybdenum within the range 4.72% to 8.6%.

The dotted line EF has been so drawn that

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all alloys whose aluminium and titanium content is within the limits indicated by the trapezium EBCF will necessarily have a molybdenum-titanium-aluminium factor of at least 16 provided that the molybdenum content is at least 6.12%.

Alloys, however, whose aluminium and titanium content is within the limits indicated by the trapezium AEFD will have a molybdenum-titanium-aluminium factor of more or less than 16 according to how much molybdenum there is in the alloy.

Particularly satisfactory alloys for use in the manufacture of jet pipes are obtained when the said alloys have an aluminium-titanium content within the parallelogram GHIJ, G corresponding to 0.6% Al and 1.9% Ti, H corresponding to 0.6% Al and 2.2% Ti, I corresponding to 0.35% Al and 2.45% Ti and J corresponding to 0.35% Al and 2.15% Ti.

Since, in accordance with the present invention, the molybdenum-titanium-aluminium factor of the alloys is at least 16, the alloys whose aluminium-titanium content is indicated by the points G, H, I, J will respectively have molybdenum contents of at least 7.2%, at least 6.0%, at least 5.5% and at least 6.7%.

It will be noted that the combined aluminium and titanium content of all alloys falling within the parallelogram GHIJ is in the range 2.5—2.8%. Such alloys may be treated by a

process comprising solution treating the alloy from 10 to 15 minutes at 1060°—1180° C.

Alloys according to the present invention may be melted in air or in a vacuum and then rolled out into a sheet in the normal way after which they are preferably heat treated by being solution treated and thereafter aged for 4 to 16 hours at from 700° C. to 800° C. In the case of alloys whose aluminium-titanium content is such that they fall within the rectangle AEKD, and whose titanium content is therefore from 1.7—2.1%, the solution treatment may be from 10 to 30 minutes at from 1080—1120° C. Alloys whose aluminium-titanium content falls within the rectangle EBCK, however, and whose titanium content is therefore from 2.1—2.45%, may be prepared by a process comprising solution treating the alloy from 10 to 15 minutes at 1050—1120° C.

Alloys according to the present invention can be argon arc-welded or seam welded, and heavy sections may be butt welded. If a filter rod is required, as may be the case with comparatively thick sheets (say more than 0.028 inch), it may be of the same alloy.

An alloy according to the present invention, referred to below as alloy B and having a molybdenum-titanium-aluminium factor of 16.66 may be compared with a commercial sheet alloy at present in use for the inner wall of jet pipes and known as Alloy S.

Composition of Alloys by weight:—

Alloy B		Alloy S
Chromium	21.00%	19.8%
Titanium	2.41%	2.3%
Aluminium	0.51%	1.2%
Cobalt	20.00%	0.6%
Manganese	0.40%	0.3%
Silicon	0.30%	0.5%
Molybdenum	6.00%	not present
Iron	0.50%	0.9%
Carbon	0.04%	0.1%
Sulphur	0.005%	0.007%
Nickel	Remainder	Remainder

Alloy B was solution treated from 10 to 15 minutes at 1120° C., argon arc welded and aged for 16 hours at 780° C.

Alloy S was solution treated from 10 to 15 minutes at 1080° C., argon arc welded and

aged for 4 hours at 750° C.

The welded portions were then tested in accordance with the four tests set out above. Both were found to comply with tests 3 and 4. Tests 1 and 2 gave the following results:

Alloy	Percentage Elongation at 775° C. (test 2 above)	Thermal cycles to failure; 20° to 775° C. (tested on apparatus as in test 1 above)
Alloy B	8 per cent	510
Alloy S	1 per cent	8

It will be noted that the permissible amounts of aluminium and titanium in the alloys of the present invention lie within very narrow ranges. An alloy F was made to demonstrate how critical are the limits of these ranges, the alloy F having the same composition as Alloy B except that its molybdenum-titanium-aluminium content by weight was as follows:

10	Molybdenum	6.07%
	Titanium	1.51%
	Aluminium	0.21%

Alloy F therefore contained somewhat too little aluminium and titanium.

15 Alloy F was subjected to the four tests described above and was very satisfactory so far as tests 1 and 2 were concerned since it remained unbroken after 3,250 thermal cycles and had a percentage elongation at 775° C. of 20 20. Alloy F, however, failed tests 3 and 4 and was therefore unsatisfactory in respect of its creep resistance and tensile strength.

WHAT WE CLAIM IS:—

1. An alloy having the following percentage composition by weight:—

30	Chromium	19.0—23%
	Cobalt	12.0—25%
	Molybdenum	4.72—8.6%
	Titanium	1.7—2.45%
	Aluminium	0.3—0.74%
	Manganese	0.2—0.6%
	Silicon	0.1—0.5%

and optionally up to 0.06% carbon, up to 1.0% iron, and up to 0.5% zirconium, the balance being nickel apart from impurities and residuals from de-oxiders, the molybdenum-titanium-aluminium factor of the alloy, as hereinbefore defined, being at least 16.

2. An alloy as claimed in claim 1 in which the alloy contains 4.72—6.1% by weight of molybdenum.

3. An alloy as claimed in claim 1 in which the alloy contains 5.5—6.5% by weight of molybdenum.

4. An alloy as claimed in any preceding claim in which the alloy contains 1.7—2.1% by weight of titanium.

5. An alloy as claimed in any of claims 1—3 in which the aluminium content of the alloy is from 0.35—0.6% by weight, the titanium content is from 1.9—2.45% by weight, and the combined aluminium-titanium content

is from 2.5—2.8% by weight.

6. An alloy as claimed in any preceding claim and containing up to 0.01% by weight of sulphur. 55

7. An alloy as claimed in claim 6 and containing up to 0.005% by weight of sulphur.

8. An alloy as claimed in any preceding claim in which the alloy contains 18—21% by weight of cobalt. 60

9. A method of treating an alloy as claimed in any preceding claim comprising solution treating the alloy.

10. A method of treating an alloy as claimed in claim 9 in which the alloy is aged for solution treating it. 65

11. A method as claimed in claim 10 in which the alloy is aged for 4 to 16 hours at from 700° C. to 800° C. 70

12. A method of treating an alloy as claimed in claim 4 comprising solution treating the alloy from 10 to 30 minutes at from 1080—1120° C., and thereafter aging it from 4 to 16 hours at from 700° to 800° C. 75

13. A method of treating an alloy as claimed in claim 1 and whose titanium content is from 2.1—2.45% the said method comprising solution treating the alloy from 10 to 15 minutes at 1050—1120° C. 80

14. A method of treating an alloy as claimed in claim 5 comprising solution treating the alloy from 10 to 15 minutes at 1060° to 118° C. 85

15. An alloy as claimed in claim 1 and having substantially the composition of Alloy B. 90

16. A method of treating an alloy as claimed in claim 15 comprising solution treating the alloy from 10 to 15 minutes at 1120° C. and aging it for 16 hours at 780° C. 95

17. An alloy when treated by the method claimed in any of claims 9—14 and 16. 95

18. A sheet of an alloy as claimed in any of claims 1—8, 15 and 17. 95

19. An article formed by welding together a number of sheets of the alloy claimed in any of claims 1—8, 15 and 17. 100

20. A jet pipe formed from an alloy claimed in any of claims 1—8, 15 and 17.

21. An extruded length of the alloy claimed in claim 1.

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PROVISIONAL SPECIFICATION

No. 38217 A.D. 1958

Nickel-Chromium-Cobalt Alloys

We, ROLLS-ROYCE LIMITED, a British Company, of Nightingale Road, Derby, do hereby declare this invention to be described in the following statement:—

5 Difficulties are experienced in the manufacture of the inner walls of jet pipes of modern gas turbine engines. Such walls must be made of an alloy which will stand up to repeated and rapid heating up to and cooling from temperatures which have today increased to about 10 800° C. The alloy must have a high resistance to oxidation, must be readily weldable, possess a high creep strength and have good tensile strength and ductility to stand up to the 15 stresses involved in such pipes which may be as much as 40 inches in diameter and 20 feet

in length.

The effect of the increase of temperatures has shortened the life of the materials previously employed and stronger known alloys which the applicants have tried have shown poor ductility in or near the weld in spite of various heat treatments applied. Moreover to apply heat treatment to the completed welded part is a matter of some difficulty in view of the dimensions of the pipe.

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The applicants have now discovered that by making a selection of constituents within the following ranges an alloy can be made which will have the required characteristics as demonstrated by its passing the under-mentioned tests.

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Composition of alloy:

Chromium	19.0 — 23.0 per cent of the alloy by weight		
Cobalt	12.0 — 25.0	„	„
Molybdenum	3.0 — 6.10	„	„
Titanium	1.7 — 2.10	„	„
Aluminium	0.3 — 0.74	„	„
Manganese	0.2 — 0.6	„	„
Silicon	0.1 — 0.5	„	„
Carbon not exceeding	0.06	„	„
Iron not exceeding	1.0	„	„
Nickel	Remainder apart from impurities and residuals from deoxidisers		

35 Zirconium may be present up to 0.5 per cent but is preferably kept low, or is absent from the alloy.

Carbon and iron will be present due to the use of commercial alloys used in making up our alloys. We prefer to keep them as low as possible.

TESTS.

1. Heating and Cooling:

45 The welded sheet prepared for test is subjected in the weld area to heating for 10 seconds followed by natural cooling for 50 seconds while stressed at a constant load of 7.8 tons per square inch. The weld area must withstand at least 500 cycles of heating up to any temperature not exceeding 800° C. and 50 cooling down again without failure.

An example of apparatus for carrying out this test is illustrated diagrammatically in the accompanying drawing in which 10 is the test piece 4 inches wide consisting of two pieces of sheet welded together at 11 suspended at the top on a rod 12 and supporting at the bottom, by a rod 18, a weight 14. A burner 15 fed through a pipe 16 with mixed air and gas coming through pipes 17 and 18 respectively discharges a number of jet flames against the weld area. Around the burner is a cylinder 19 having a cut away portion 20. This is rotated so that the exposure of the weld to the flame lasts for 10 seconds and for the remainder of the rotation of the cylinder which lasts for 50 seconds the weld is masked by the cylinder from the flame. The thermocouple

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shown at 21 records the temperature of the weld. In this way the test piece can be brought up to the temperature desired cooled naturally and heated again rapidly to the test temperature.

2. Ductility:

The ductility of the welded test piece after being aged and stressed with the weld at right angles to the axis of pull shall be not less than 5.0 per cent elongation after fracture of a standard size test piece at a test temperature of 775° C. measured when cold on a 1.0 inch gauge length across the weld.

15 By standard size test piece is meant a piece 0.75 inches wide with a parallel section 3 to 3.5 inches long streamlined into ends of 1.25 inches.

3. Creep:

Under a continuous loading test the material shall deform by not greater than 1.0 per cent strain after 100 hours at 775° C. under a stress of 7.8 tons per square inch.

4. Tensile Strength:

The tensile strength after 30 minutes soaking and then tested at 775° C. shall be not less than 30 tons per square inch with a 0.1 Proof stress of at least 14.5 tons per square inch.

The alloy which we have selected will pass all the above tests.

The alloy may be melted in air or in a vacuum and then rolled out into a sheet in the normal way after which it is preferably heat treated by being solution treated at from 1080 to 1120° C. for 10 to 30 minutes after which it may be aged for 4 to 16 hours at from 700° to 800° C.

The alloy can be argon arc-welded. Thin sheets may be butt welded. If a filler rod is required as may be the case with comparatively thick sheets (say more than 0.028 inches). They may be of the same alloy.

Our alloy may be compared with a commercial sheet alloy at present in use for the inner wall of jet pipes and known as Alloy S.

Composition of alloys:

Our Alloy				S. Alloy
Chromium	21.00	per cent		19.8 per cent
Titanium	1.75	„	„	2.3 „ „
Aluminium	0.45	„	„	1.2 „ „
Cobalt	20.00	„	„	0.6 „ „
Manganese	0.40	„	„	0.3 „ „
Silicon	0.30	„	„	0.5 „ „
Molybdenum	6.00	„	„	not present
Iron	0.50	„	„	0.9 per cent
Carbon	0.04	„	„	0.1 „ „
Nickel	Remainder			Remainder

Our alloy was solution heated from 10 to 15 minutes at 1120° C., argon arc welded and aged for 16 hours at 780° C.

50 Alloy S was solution heated from 10 to 15 minutes at 1080° C. argon arc welded and

aged for 4 hours at 750° C.

The welded portions were then tested in accordance with the four tests set out above. Both were found to comply with tests 3 and 4. Tests 1 and 2 gave the following results:

Alloy	Elongations per cent at 775° C. (test 2 above)	Thermal cycles to failure: 20° to 775° C. (Tested on apparatus as in Test 1 above)
Our alloy	11 per cent	1,020
S alloy	1 per cent	8

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PROVISIONAL SPECIFICATION

No. 16721 A.D. 1959

Nickel-Chromium-Cobalt Alloys

We, ROLLS-ROYCE LIMITED, a British Company, of Nightingale Road, Derby, do hereby declare this invention to be described in the following statement:—

5 In the specification of our co-pending application No. 38217/58 we disclosed a range of nickel-chromium-cobalt alloys which have properties such as to make them particularly suitable for use in the manufacture of jet

10 pipes of gas turbine, jet reaction engines.

We have now discovered certain additional nickel-chromium-cobalt alloys which, although outside the range disclosed in the said co-pending application have the like properties.

15 According therefore to the present invention there is provided an alloy having the following percentage composition by weight:—

	Cobalt	12.0—25%
	Chromium	19.0—23%
20	Molybdenum	3.0—6.10%
	Titanium	1.7—2.45%
	Aluminium	0.3—0.74%
	Manganese	0.2—0.6%
	Silicon	0.1—0.5%
25	Carbon	not exceeding 0.06%
	Iron	not exceeding 1.0%

the balance being nickel apart from impurities and residuals from oxidisers, the molybdenum-titanium-aluminium factor, as hereinafter defined, being less than 16.

30 The term "molybdenum-titanium-aluminium" factor, as used in this specification, is to be understood to indicate the factor obtained by adding together the percentage of molybdenum, twice the percentage of aluminium and four times the percentage of titanium present in the alloy.

35 Thus, for example, if an alloy in accordance with the present invention contains 6.1% molybdenum, 0.4% aluminium, and 2.2% titanium, its molybdenum-titanium-aluminium factor will be

$$6.1 + 2(0.4) + 4(2.2) \\ = 6.1 + 0.8 + 8.8 \\ = 15.7$$

40 Preferably the aluminium content is from 0.35—0.6% and the titanium content is from 1.9—2.45%.

45 In the accompanying diagram, which has been called Figure 2 to distinguish it from the diagram accompanying co-pending application No. 38217/58, the rectangle ABCD defines the

limits of the aluminium and titanium content of alloys according to the invention.

55 The dotted line EF has been so drawn that all alloys whose aluminium and titanium content is within the limits indicated by the trapezium AEFD and whose molybdenum content is from 3.0—6.10% by weight will necessarily have a molybdenum-titanium-aluminium factor of less than 16.

60 Alloys, however, whose aluminium and titanium content is within the limits indicated by the trapezium EBCF and whose molybdenum content is from 3.0—6.10% by weight, will have a molybdenum-titanium-aluminium factor of more or less than 16 according to the amount of molybdenum in the alloy. Certain alloys in the trapezium EBCF will therefore be outside the scope of the present invention.

65 Particularly satisfactory alloys for use in the manufacture of jet pipes are obtained when the said alloys have an aluminium-titanium content within the parallelogram GHIJ, G corresponding to 0.6% Al and 1.9% Ti, H corresponding to 0.6% Al and 2.2% Ti, I corresponding to 0.35% Al and 2.45% Ti and J corresponding to 0.35% Al and 2.15% Ti. Such alloys may be prepared by a process comprising solution heating the alloy from 10 to 15 minutes at 1060° C.

70 Alloys according to the present invention whose aluminium-titanium content is such that they fall within the rectangle AEDK were disclosed in the co-pending application No. 38217/58 and, as disclosed therein, may be prepared by a process comprising solution heating the alloy from 10 to 30 minutes at 1060—1120° C. Alloys according to the present invention whose aluminium-titanium content falls within the rectangle EBCK, however, may be prepared by a process comprising solution heating the alloy from 10 to 15 minutes at 1050—1100° C.

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form by more than 1% after 100 hours at
775° C. under a stress of 7.8 tons per square
inch.

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the Original on a reduced scale

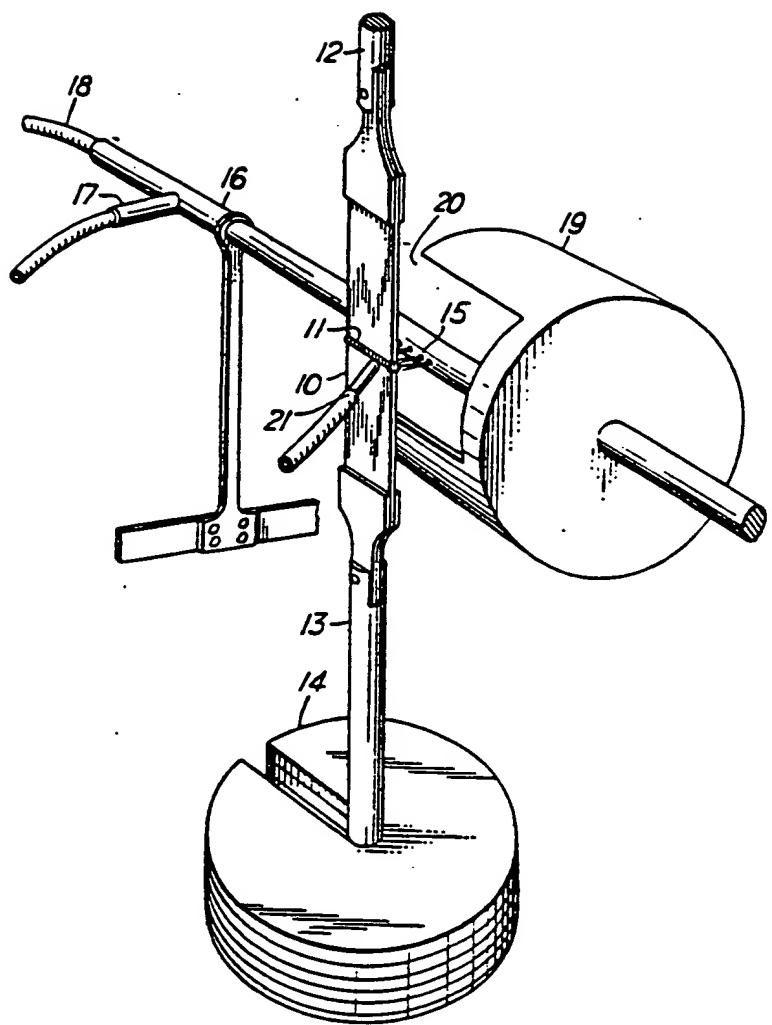


Fig. 1.

880805

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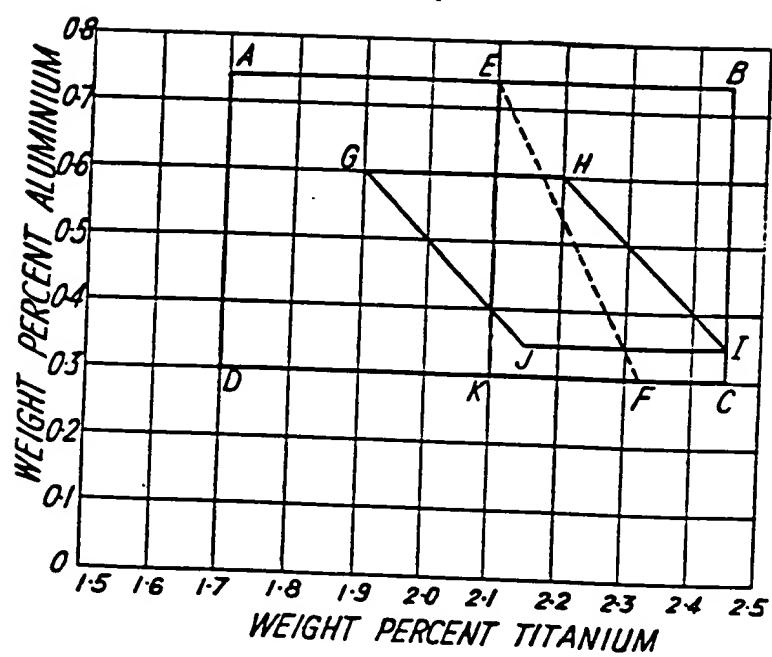


Fig. 2.